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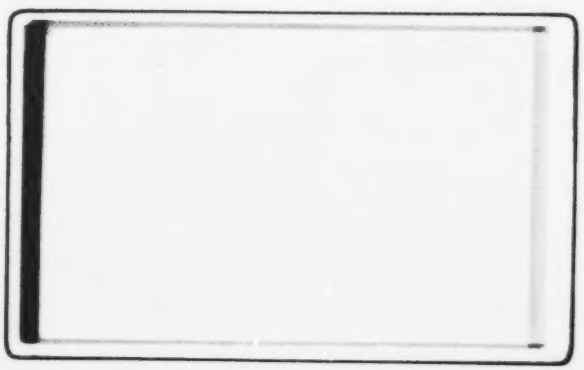

Environmental Protection Service

Service de la protection de l'environnement

CONTAMINATION BY PESTICIDES
OF THE LA SALLE AND
ASSINIBOINE RIVERS,
MANITOBA, CANADA

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Contamination by Pesticides of the La Salle and Assiniboine Rivers, Manitoba, Canada

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ABSTRACT

The La Salle River is located within an intensively farmed fertile basin in south-central Manitoba. The natural flow in this stream is being augmented with water pumped from the Assiniboine River in an attempt to provide an adequate supply for domestic consumption, livestock watering and irrigation purposes. Concerns with regard to the presence of agricultural pesticides in this stream led to the initiation of this investigation. Water samples were collected from seven locations on the La Salle River and from two sites on the Assiniboine River once per month from August to December, 1984. Representative forage fish, aquatic macrophyte and bottom sediment samples were collected on one occasion in August, 1984. All samples were analysed for bromoxynil, 2,4-D, dicamba, diclofop-methyl, MCPA, triallate and trifluralin. Dicamba, bromoxynil, diclofop-methyl and 2,4-D were quantified in water samples collected from the La Salle River at concentrations ranging from 0.10 to 3.98 ug/L. These concentrations do not pose a significant threat to humans; the data is inadequate to determine the effects to aquatic organisms. Trifluralin and triallate were not detected in the water column but were quantified in forage fish and bottom sediment samples collected from both the La Salle and Assiniboine rivers, suggesting that even at low levels, these pesticides bioconcentrate in the biota. MCPA was not detected in any medium. These agricultural pesticides were not detected in aquatic macrophytes.

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1. Introduction

Agricultural pesticides are widely used within Manitoba to reduce crop damage due to weed competition and due to ingestion and decay by insect and microbiological pests. Such pesticides can reach surface waters by a variety of pathways. These include overland drainage following intense precipitation events and snow melt, internal soil drainage, direct accidental application to watercourses, accidental releases during spray equipment rinsing and filling operations and transport from the soil surface by wind erosion.

Central to the successful management of surface water quality is knowledge concerning the distribution and effect of all such substances within Manitoba's aquatic systems. While the occurrence of conventional pollutants such as trace metals and other inorganic constituents has been well documented through routine ambient water quality monitoring activities and site specific intensive studies, the distribution of pest control products is less well understood. In a previous study, Williamson (1984) examined the La Salle and Assiniboine rivers for the presence of agricultural pesticides in the vicinity of Elie, Manitoba. Williamson (1984) sampled two sites on the La Salle River on 16 occasions between April, 1983 and March, 1984; two sites on the Assiniboine River at monthly intervals between

May, 1983 and March, 1984; and three surface water pools on one occasion. Residues of triallate, trifluralin, azinphos-methyl, dicamba, MCPA, diclofop-methyl and 2,4-D in surface water were observed. A study examining the occurrence of many of these same substances in the Ochre and Turtle rivers in the vicinity of Dauphin, Manitoba has also been carried out by Muir and Grift (in prep.).

The La Salle River is used extensively as a municipal domestic supply, for irrigation purposes and for livestock watering. Concerns about the presence of agricultural pesticides in this stream led to the initiation of this investigation. The purpose of the investigation was to determine the distribution of agricultural pesticides within the entire reach of the La Salle River, and to assess the implications of any positive results. The Assiniboine River downstream of Portage la Prairie was also examined as water from the lower reaches of the Assiniboine River is being intermittently used to augment La Salle River discharges in order to increase flow and decrease salinity for improved water quality. The study focused on the compounds previously identified in the La Salle River near Elie, Manitoba (Williamson, 1984) and on other compounds of concern identified during an intensive pesticide use survey conducted within the watershed (Cowan and Therrien-Richards, 1986).

2. The Study Area

The La Salle River watershed (Figure 1) is located within south central Manitoba and is approximately 2150 km^2 in area (Fedoruk, 1970). Most soils within the watershed consist of Black Chernozemic and Humic Gleysol soils developed on moderately clayey to strongly calcareous deposits. The Black Chernozemic soils are well-drained, have moderate run-off and moderate permeability. The soil textures vary from very fine sandy loams to clay loams. These soils have a neutral to slightly basic pH. The Humic Gleysol soils are poorly drained with a high proportion of clay particles. These soils are slightly acid to neutral in pH. In the upper La Salle River watershed, the dominant soils are also Black Chernozemic, with lesser intrusions of Humic Gleysol soils which have developed on sandy deposits (Clayton et al., 1977).

The Black Chernozemic soils which predominate in the La Salle River watershed are relatively high in productivity and are well-suited for the production of field crops. The area, therefore, is intensively farmed. Cereal grains, special crops such as various oilseeds, forage and some vegetable crops predominate. Significant livestock production within the watershed also occurs, although grazing on native pasture is mostly restricted to

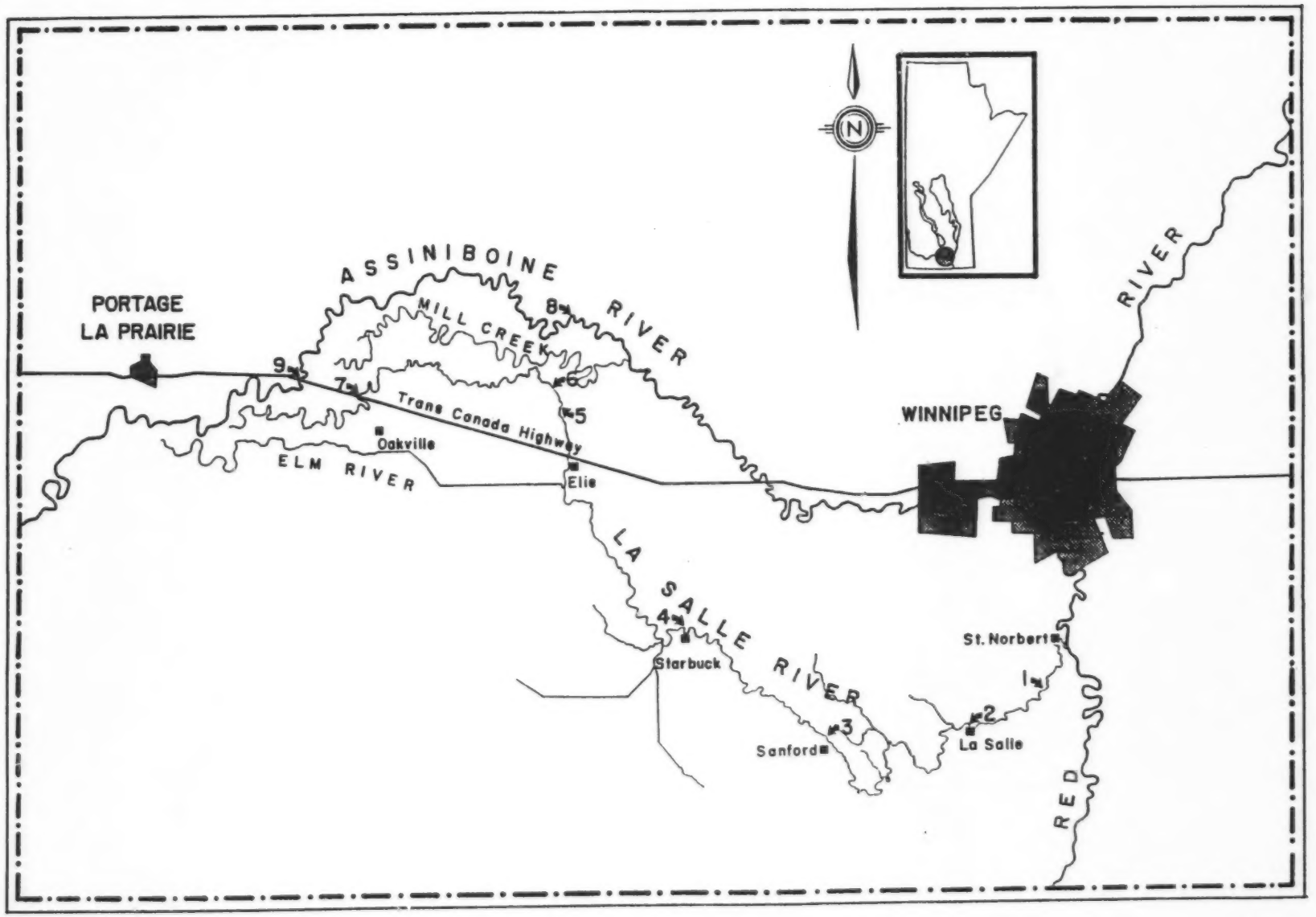

Figure 1. La Salle River study area.

very coarse textured sandy or stony lands, or to poorly drained meadow areas where Gleysolic soils occur.

The La Salle River is a slow moving, meandering stream flowing along a paleochannel once occupied by the Assiniboine River. The La Salle River joins the Red River at the southern boundary of the City of Winnipeg, Manitoba. Discharge reaches maxima during spring melt water runoff. Historical mean flows observed during April and May are 1.34 m^3/s and 0.971 m^3/s, respectively (Water Survey of Canada, 1983).

Numerous dams are located along the entire length of the La Salle River. Typically during the summer low flow periods, the La Salle River becomes a series of elongated quiescent reservoirs. Recent year-round diversion of water from the Assiniboine River has augmented the natural La Salle River flows by approximately 0.70 m^3/s at the point of diversion. This flow augmentation has also increased the natural discharges of Mill Creek and Elm River, both tributary to the La Salle River, by 0.28 m^3/s and 0.14 m^3/s, respectively. Flow augmentation began in November, 1984.

3. Methods

3.1 Agricultural Chemical Use Survey 1984

In order to maximize the resources available for the project, it was important to focus on those compounds most widely used and those with the greatest potential for reaching and impairing the quality of the La Salle River. To this end, a farm use survey of agricultural chemicals was conducted during July and August, 1984 (Cowan and Therrien-Richards, 1986). The results of this survey were used in part to select the following pesticides for sampling and analysis in this study: dicamba, bromoxynil, 2,4-D, MCPA, trifluralin, triallate and diclofop-methyl.

3.2 Surface Water, Surficial Bottom Sediments, Aquatic Macrophytes and Forage Fish Sampling

Surface water samples were collected from the La Salle and Assiniboine rivers from August, 1984 to December, 1984, at approximately 30-day intervals. Nine sampling locations were selected (Figure 1) and are described in Table 1.

Table 1. Description of pesticide residue sampling locations in the La Salle and Assiniboine rivers (August to December, 1984)

Site Number	Stream	Description
1	La Salle River	Immediately upstream of the Waverley Street dam at La Barriere Park
2	La Salle River	Hwy. 330 near La Salle
3	La Salle River	Hwy. 334 near Sanford
4	La Salle River	Hwy. 332 near Starbuck
5	La Salle River	3.2 km north, 0.8 km west of Elie (Hwy. 248)
6	La Salle River	0.8 km north, 0.8 km west of site #5
7	La Salle River	Trans Canada Highway near Oakville
8	Assiniboine River	Hwy. 248 north of Elie
9	Assiniboine River	Trans Canada Highway east of Portage la Prairie

Water samples destined for organic analyses were collected in 1 L Boston round bottles pre-cleaned by the Environmental Protection laboratory in Edmonton using pesticide-grade acetone and dichloromethane, followed by heat treatment. Samples were obtained during open water by wading to a location near mid-stream (or at least 5 m offshore). The sample bottle was then immersed approximately 0.5 m below the water surface from a region that

had not been disturbed by the sampler. One sample was collected at each site. During ice cover, samples were obtained from approximately 0.5 m below the ice surface. Twenty-five mL of dichloromethane were added to the sample bottle immediately after sample collection. The samples were chilled and shipped on ice via air freight to the Environmental Protection laboratory, Edmonton, Alberta, for analyses.

Surficial bottom sediment samples were collected on one occasion in August, 1984 from all sampling locations. The bottom sediment samples from the La Salle River (sampling locations 1 through 7) were collected with the use of a standard Wildco Ekman dredge. Samples were collected at three equidistant points across the stream width. The samples were consistently identified with sample "a" located closest to the right hand shore when facing downstream. Approximately 100 g of the top 3 cm of substrate were carefully removed and placed in glass sampl. containers rinsed with pesticide-grade acetone and dichloromethane, then heat-treated. Bottom sediment samples collected from the Assiniboine River (sampling locations 8 and 9) were collected by hand, from fine-grained deposits located on the lee side of midstream obstructions such as sand bars or rocks. The predominant bottom substrate of the Assiniboine River at the sampling locations consisted of well-sorted sand and gravel, thus precluding

the collection of fine-grained sediment at regular stream width intervals.

Aquatic macrophyte samples were collected on one occasion in August, 1984 from La Salle River sites 1,2,4 and 6. Each sample consisted of approximately 100 g of pond milfoil (Myriophyllum sp.). The samples were thoroughly rinsed in stream water to remove all attached sediments, then were placed in pre-cleaned glass sample containers. Aquatic macrophytes were not present near the Assiniboine River sampling location 8 because of the nature of the bottom substrate and the turbulent stream flow.

Small forage fish samples from sites 1,2,4,6 and 8 were collected by seine nets and basket-type minnow traps. Approximately 100 g of whole fish were presented for analyses in pre-cleaned glass sample containers. It was not possible to use the same fish species for all analyses as no one species was present at all sites. The species composition of the forage fish samples are described in Table 2.

Bottom sediment, aquatic macrophyte and forage fish samples were immediately chilled following collection, then stored frozen until analyses were performed by the Environmental Protection laboratory, Edmonton, Alberta.

Table 2. Fish species collected at sampling locations

Sampling Location	Species
1 - La Salle River	Brown bullhead (Ictalurus nebulosus) (young of the year)
2 - La Salle River	Brown bullhead (young of the year)
4a - La Salle River	Brook stickleback (Culaea inconstans)
4b - La Salle River	Central mudminnow (Umbra limi)
4c - La Salle River	Brown bullhead
6a - La Salle River	Central mudminnow
6b - La Salle River	Brook stickleback
8 - Assiniboine River	Silver chub (Hybopsis storeriana) Stonecat (Noturus flavus) Channel catfish (Ictalurus punctatus) Brown bullhead

3.3 Pesticide Analyses

All samples were analyzed for residues of dicamba, bromoxynil, 2,4-D, MCPA, trifluralin, triallate and diclofop-methyl. Details of sample container preparation, extraction and analytical methodologies are described by Birkholz and Schwanbeck (1985). Briefly, the water samples were acidified and then extracted with diethyl ether. Each extract was divided in two; one

half was set aside for neutral herbicide analysis, and the other for methylation and subsequent acid herbicide analysis. The extracts were cleaned using Florisil columns. The resulting fractions were then preconcentrated to an appropriate volume and analyzed using gas chromatographs equipped with Ni^{63} electron-capture detectors.

Sediment, fish and macrophyte samples were homogenized, extracted firstly with acetone to yield a neutral fraction, and secondly, with acidified methanol, to yield an acid fraction. After work-up and appropriate concentration, the extracts were analyzed for pesticides, also using gas chromatographs equipped with Ni^{63} electron-capture detectors. A cleanup of extracts was made using silica gel chromatography, Florisil chromatography, sulfur removal and gel permeation chromatography. The sediment samples were also analyzed using mass spectrometry.

3.3.1 Quality Control - Water Samples

Three samples of North Saskatchewan River water were fortified with herbicides and extracted using two extraction methods. One method involved extraction with 25 percent diethyl

ether in dichloromethane. This method, although yielding higher recovery rates, resulted in emulsion problems. The second method involved extraction with 100 percent diethyl ether; emulsion problems were greatly reduced and consequently, this method was used primarily for the extraction of the La Salle River water samples.

To test sample preservation, a fortified water sample was submitted to field personnel, preserved and returned to the laboratory. The recoveries for the pesticides analyzed are reported in Table 3, along with the detection limit for each pesticide. These recovery values are consistent with the values obtained for the fortified North Saskatchewan River water samples extracted with 100 percent diethyl ether, indicating that sample preservation with dichloromethane was effective.

Table 3 Recoveries obtained for herbicides from fortified field blank

Herbicide	Detection Limit (ug/L)	Fortification Level (ug/L)	Level Recovered (ug/L)	Percent Recovery
Bromoxynil	0.05	0.111	0.065	59
2,4-D	0.20	1.130	0.983	87
Dicamba	0.10	0.240	0.187	78
Diclofop-methyl	0.50	0.980	0.921	94
MCPA	10.0	19.4	14.0	72
Triallate	0.10	0.265	0.217	82
Trifluralin	0.10	0.214	0.133	62

3.3.2 Quality Control - Sediment, Fish and Macrophyte Samples

Known amounts of herbicides were added to two bottom sediment samples from the Saskatchewan River, to one sample of 2.5 - 5 cm long minnows purchased commercially and to one sample of water milfoil from a slough in Alberta. These samples were carried through the methodology described previously to determine recovery efficiencies for the sediment, fish and macrophyte samples. These data are summarized in Table 4.

Table 4. Recoveries obtained for herbicides from fortified samples of sediment, fish and macrophytes

Herbicide	Fortification Level (ng/g)	Detection Limit (ng/g)	Percent Recovery			
			Sediments		Fish	Macrophyte
			Sample 1	Sample 2		
Bromoxynil	2.08	0.43	81	*	90	100
2,4-D	19.4	3.8	107	*	82	118
Dicamba	5.57	1.3	114	96	70	82
Diclofop-methyl	15.9	8.2	82	60	39	74
MCPA	338.	65.	68	91	*	78
Triallate	8.53	2.7	72	100	65	55
Trifluralin	3.68	1.4	133	103	*	120

* Interference

4. Results and Discussions

Cowan and Therrien-Richards (1986) found that the herbicides used most extensively in the La Salle River area were difenzoquat, triallate, dicamba, bromoxynil, MCPA, diclofop-methyl, sethoxydim, trifluralin and 2,4-D. In addition, significant quantities of the insecticides terbufos and carbofuran were applied in the area surveyed.

Analysis by the Environmental Protection laboratory in Edmonton, Alberta was not possible for all of the herbicides used in the La Salle River area. Methodologies had not been developed by the laboratory for the analysis of sethoxydim, terbufos and carbofuran, and time constraints prevented the development of the necessary analytical protocols. Analysis for difenzoquat was also not carried out because replicate samples had not been collected in the field. The results obtained for each pesticide which was analysed is discussed in the following sections.

4.1 Dicamba

Dicamba, the common name for 3,6-dichloro-o-anisic acid, was

developed to control annual and perennial broadleaf weeds in cereals. It is readily absorbed by leaves and roots, and translocated. As a postemergent herbicide, it is usually formulated with other commercial herbicides such as MCPA or 2,4-D, with the dosage of dicamba in these formulations ranging from 80 to 130 grams of active ingredient per hectare (Glasshouse Crops Research Institute, 1979).

The major pathway for loss of residues of dicamba in soil is metabolism by soil organisms. The rate of biodegradation increases with temperature and increasing soil moisture. Under optimal conditions, dicamba has a half-life of less than 14 days in soil. With conditions of low moisture in soil and small amounts of precipitation, dicamba persists in the soil much longer. When soil moisture exceeds 50 percent, biodegradation reaches a maximum and then declines with increasing moisture. Loss of dicamba from the soil profile then occurs by leaching. Maximum leaching was observed with large volumes of percolating liquid. Dicamba was leached out of a zone of activity in a humid soil in a period of 3 to 12 weeks (Herbicide Handbook Committee, WSSA, 1983). The concentration of dicamba in soil therefore would be affected by the total seasonal precipitation and would depend on the duration, frequency and severity of individual precipitation events.

Dicamba was detected in the 0.1 to 4 ppb range in the surface water samples from the La Salle River (Table 5). Most applications of dicamba would be made in late May to mid-June in Manitoba, when crops are in the 2-5 leaf stage. Assuming a 3 to 12 week leaching time as mentioned earlier, residues of dicamba in surface waters should initially be detectable from late June to mid-September. Sampling in June and July was not conducted. The results from the La Salle River obtained in August were higher than in subsequent months with the exception of station one where levels peaked in September. Detectable levels of dicamba in the La Salle River persisted through December.

Table 5. Concentration of dicamba (ug/L) in surface waters

Sampling Date	Station No. 1	2	3	4	5	6	7	8	9
13 Aug 84	0.30	0.26	0.36	ND	ND	ND	ND	ND	ND
18 Sept 84	0.40	0.13	0.15	0.20	ND	ND	ND	ND	ND
17 Oct 84	0.10	0.12	0.12	0.20	ND	ND	ND	ND	ND
13 Nov 84	ND[1]	0.10	ND	ND	NR[2]	0.10	ND	ND	ND
18 Dec 84	0.11	0.15	0.13	ND	0.12	NR	ND	ND	ND

1. ND = Not Detected
2. NR = No Result

Dicamba was not detected in the Assiniboine River. This may be because of increased dilution as a result of the much greater volume of water in the Assiniboine River as compared to the La Salle River. Dicamba was also not detected in the sediment, fish or macrophyte samples taken from either the La Salle or the Assiniboine rivers.

The residues of dicamba detected in the La Salle River would not pose an acute hazard to aquatic organisms or water users. The Glasshouse Crops Research Institute (1983) reported 96-hour LC_{50} for technical dicamba of 28 mg/L and 23 mg/L respectively for rainbow trout (Salmo gairdneri) and bluegill (Lepomis macrochirus). The 48-hour LC_{50} for dicamba as the methyl ammonium salt was reported to be 465 mg/L for small carp (Cyprinus carpio)(Herbicide Handbook Committee, WSSA, 1983). Oral LD_{50} values for dicamba as the dimethylamine salt ranged from 566 mg/kg for the guinea pig to 1028 mg/kg for the rat (Herbicide Handbook Committee, WSSA, 1983). Dicamba is not stored in tissue but is excreted rapidly. Ivie and Oehler (1980) reported that low-level dicamba exposure (60 mg/L dietary) of ruminants through contaminated feed or water, would probably not result in appreciable retention of residues by edible tissue or their secretion into milk. Yu et al. (1975) also reported that dicamba did not magnify in food chain organisms.

The highest level detected, 4 ug/L, is well below the maximum level of 200 ug/L calculated by Williamson (1984) in order to afford adequate long-term protection to aquatic life. The values are also lower than the no-effect level in drinking water of 9 ug/L recommended by the National Academy of Sciences (1977).

4.2 Bromoxynil

3,5-dibromo-4-hydroxybenzonitrile, commonly called bromoxynil, is a contact herbicide developed to control post-emergent seedling broad-leafed weeds in cereal crops. It is applied at the rate of 280 - 560 grams of active ingredient per hectare, often in combination with 2,4-D or MCPA. Bromoxynil is not readily translocated once absorbed by the plant. In soil, bromoxynil is readily degraded by microorganisms and chemical reactions, with 50 percent loss occurring in 10 days (Herbicide Handbook Committee, WSSA, 1983). The oil-soluble amine and ester resist removal from foliage by rain. The sodium salt is water soluble and can be readily removed from plant surfaces with rain.

Bromoxynil was detected in only one sample of surface water

on one sampling occasion (Table 6). Bromoxynil was not detected in the sediment, fish or macrophyte samples. Cowan and Therrien-Richards (1986) determined that bromoxynil was applied in significant quantities in the La Salle River area. Since most formulations of bromoxynil applied were the water insoluble octanoate ester, significant quantities of bromoxynil were not expected to be leached by rainwater from the site of application into surface waters.

Table 6. Concentration of bromoxynil (ug/L) in surface waters

Sampling Date	Station No. 1	2	3	4	5	6	7	8	9
13 Aug 84	ND[1]	ND	ND	ND	ND	ND	ND	ND	ND
18 Sept 84	ND	ND	ND	ND	ND	ND	ND	ND	ND
17 Oct 84	ND	ND	ND	ND	ND	ND	ND	ND	ND
13 Nov 84	ND	ND	ND	ND	NR[2]	ND	ND	ND	ND
18 Dec 84	ND	ND	ND	ND	0.10	NR	ND	ND	ND

1. ND = Not Detected
2. NR = No Result

Bromoxynil has a 96-hour LC_{50} for rainbow trout of 0.05 mg/L. The LC_{50} (96 hr) for other aquatic species ranged from 0.011 ppm for Daphnia to 0.17 ppm for goldfish. Mammals exhibited greater tolerance. Acute oral LD_{50} of 250 mg/kg and 325 mg/kg were reported for rats and rabbits respectively. Dogs receiving a daily diet of 5 mg/kg suffered no ill effects (Glasshouse Crops Research Institute, 1979).

Health and Welfare Canada (1979) has not adopted a maximum concentration of bromoxynil in drinking water. A maximum acceptable concentration of bromoxynil in surface freshwater has also not been established by either the federal government or the provinces. Williamson (1986) has however proposed that the objective concentration in Manitoba surface waters for a non-persistent or non-cumulative pollutant not exceed 0.05 of the 96 hr LC_{50}. The least tolerance to bromoxynil was exhibited by Daphnia, with an LC_{50} (96 hr) value of 0.011 ppm. This would result in an objective concentration of 0.5 ppb in Manitoba surface waters. Alberta and Saskatchewan also recommend multi-purpose water quality objectives for pesticides generally. A concentration of pesticide should not exceed 1/100 of the 48 hour TLM (50% kill of organisms in 48-hour time span) to provide reasonably safe concentrations in receiving waters (Canadian Council of Resource and Environment Ministers, 1985). Calcula-

tion of a reasonably safe concentration in receiving waters in Alberta and Saskatchewan using the LC_{50} (96 hr) for Daphnia would result in a value of 1 ppb. The value measured in the La Salle River at Station 5 of 0.10 ppb is well below both the objective concentration proposed by Williamson and the objective concentrations recommended by the provinces of Alberta and Saskatchewan, and should not pose a threat to aquatic life.

4.3. 2,4-D

2,4-D, or 2,4-dichlorophenoxyacetic acid has been used for over 35 years to control broad-leaf weeds in crops. 2,4-D is a systemic herbicide applied post-emergent at rates from 0.28 to 2.2 kg of active ingredient per hectare for crops and pastures. Various esters and salts have been marketed by many companies. The more important ester formulations are the isopropyl, 2-butoxyethyl and isooctyl esters; the dimethylamine salt is the most important salt in terms of production (Spencer, 1981).

There is considerable variation in the physical-chemical properties between the acid, salt and ester formulations. The solubility in water ranges from essentially insoluble for the low

volatile ester to a solubility of 300 g per 100 ml of water for the amine salt. Foliar absorption and leachate characteristics are also dependent on the formulation. Uptake of 2,4-D salt formulations is primarily by plant roots, whereas leaves absorb the ester formulations most readily. The insoluble esters resist washing from plants by rainwater whereas the highly soluble salts must be applied in a rain-free period lasting 4-6 hours after application for effective weed control. The 2,4-D salts are readily leached in sandy soils but will adsorb to clay and organic matter, as will the acid and ester forms (Herbicide Handbook Committee, WSSA, 1983).

Microbial degradation of 2,4-D in soil was favoured by the presence of moisture and high organic matter (Davidson et al., 1980). Rate of breakdown was also dependent on the concentration of product applied, soil pH and temperature. At recommended rates of application, the average persistence of phytotoxicity in warm moist soil was reported to be from one to four weeks (Herbicide Handbook Committee, WSSA, 1983). Leaching of 2,4-D into surface waters when applied as a postemergent in the spring would therefore be greatest if storms occurred close to the time of application. Warm weather conditions and high humidity in the spring would accelerate the degradation of the product. Frank and Sirons (1980) confirmed that residues of 2,4-D in stream

waters were detectable after precipitation events close to the time of application.

Applications of 2,4-D are also made in late fall before freeze-up for control of winter annuals. As weather conditions in the fall do not normally favour rapid degradation (National Research Council of Canada, 1978), 2,4-D is likely to persist in the soil for longer periods of time and leaching of 2,4-D by rainfall could occur several weeks after application. Fall applications in Manitoba would have been made in September and October; yet 2,4-D was quantified in the samples collected in mid-December, six to twelve weeks after application (Table 7).

Table 7. Concentration of 2,4-D (ug/L) in surface waters

Sampling Date	Station No. 1	2	3	4	5	6	7	8	9
13 Aug 84	ND[1]	0.31	ND	ND	ND	ND	0.46	ND	ND
18 Sept 84	0.62	0.30	ND	0.25	ND	0.20	ND	ND	ND
17 Oct 84	ND	0.17	ND	0.28	0.24	0.24	3.98	ND	ND
13 Nov 84	ND	0.43	ND	ND	NR[2]	0.21	ND	ND	ND
18 Dec 84	0.28	0.14	0.24	0.18	0.87	NR	ND	ND	ND

1. ND = Not Detected
2. NR = No Result

As shown in Table 7, concentrations of 2,4-D in the surface water ranged from less than 0.2 ug/L to a maximum of 4 ug/L. These data are consistent with data obtained by Inland Waters and Lands in their pesticide monitoring programs in surface waters in Western Canada (Gummer, 1979), and in a study of the distribution of 2,4-D in the Red River (Chacko and Gummer, 1980). The herbicide 2,4-D was found to be prevalent in agricultural areas in concentrations ranging from 0.1 to 4.3 ug/L. Frank et al. (1978) also reported the presence of 2,4-D in concentrations ranging from less than 0.1 to 1.6 ug/L in 39 percent of watersheds in Ontario. 2,4-D was not quantified in any of the sediment, fish or macrophyte samples from the La Salle River.

The concentrations of 2,4-D detected in surface waters are well below concentrations determined to be lethal to fish. The toxicity of various formulations of 2,4-D for fish have been summarized by the National Research Council of Canada (1978). The acid and dimethylamine formulations exhibited toxicity at concentrations greater than 100 mg/L for bluegill. The ester formulations were most toxic, with some LC_{50} (24 h) values as low as 0.9 mg/L for bluegill. However, the esters were reported by Turner (1977) and by the National Research Council of Canada (1978) to be rapidly hydrolysed to the acid in aquatic systems. Cold temperatures and acidic conditions slowed the rate of ester

hydrolysis, increasing the risk to aquatic fauna. This would be of particular concern with fall applications of 2,4-D ester formulations.

In addition to direct lethal effects on fish and aquatic invertebrates, the National Research Council of Canada (1978) reported that high levels of phenoxy herbicides could destroy aquatic vegetation, which indirectly would adversely affect fish and aquatic organisms. It was also reported that long-term exposure to sub-lethal concentrations could cause adverse impacts to aquatic organisms such as behavioural and productivity effects.

Mammals exhibit a much greater tolerance to 2,4-D than fish. The acute oral LD_{50} of the various formulations ranges from 300 to 1000 mg/kg of body weight for rats, guinea pigs and rabbits (Herbicide Handbook Committee, WSSA, 1983). Riedel (1982) reported that 2,4-D absorbed through ingestion, inhalation or skin contact was rapidly excreted in urine and would not accumulate in the body. Although the National Research Council of Canada (1978) reported that several studies indicated that 2,4-D was of low toxicity to mammals, limited data suggested that phenoxy compounds including 2,4-D may have teratogenic potential.

To protect aquatic life and wildlife, the province of Ontario has recommended that the maximum value for 2,4-D in surface water not exceed 4 ug/L (Canadian Council of Resource and Environment Ministers, 1985). In drinking water, Health and Welfare Canada (1979) has recommended a maximum allowable concentration of 2,4-D of 100 ug/L and an objective concentration of less than or equal to 1 ug/L in its 1978 guidelines. The levels of 2,4-D which were found in the La Salle River were all significantly lower than the maximum allowable concentration and, with the exception of one value, were also below the more stringent objective concentration. These current residual levels in water should not pose a hazard to human or animal health, or to the aquatic community.

4.4 MCPA

MCPA, or 2-methyl-4-chlorophenoxyacetic acid is a selective foliage broadleaf herbicide, similar to 2,4-D. Manitoba Agriculture (1986) recommends MCPA for control of broadleaf weeds in cereal crops, flax, peas, forage grasses, seedling legumes and cover crops. MCPA is reported by the Herbicide Handbook Committee, WSSA, (1983) to be more selective than 2,4-D when applied

at equal rates on cereals, legumes and flax. The application rate varies from 0.13 to 1.2 kg of acid equivalent per hectare with water as the usual carrier. MCPA is commercially available as the water soluble potassium, sodium and dimethylamine salts, and as the water insoluble ethyl, butyl, isooctyl and butoxyethyl esters. MCPA is also available in combination with mecoprop, dicamba, bromoxynil and 2,4-D.

The absorption characteristics of MCPA by the plant are similar to 2,4-D; both products are absorbed through leaves or roots. To maximize weed control, the water-soluble salts must be applied in a rain-free interval of 4 - 6 hours. The ester formulations only require a rain-free interval of 2 - 3 hours after application to ensure no reduction in control. Once absorbed, the MCPA is readily translocated in the plant. At recommended rates of application, MCPA will persist in the soil up to 1 month in moist conditions and up to 6 months in drier conditions (Herbicide Handbook Committee, WSSA, 1983).

MCPA, as well as other phenoxy herbicides, is considered to be relatively non-toxic to mammals and birds (National Research Council of Canada, 1978). MCPA was reported to have LD_{50} values ranging from 700 to 1200 mg/kg of body weight for rats, depending on the formulation. LD_{50} values of 550 and 560 mg/kg for mice

were reported for the sodium salt and the amine respectively. Researchers, however, have reported that MCPA produced fetal malformations and other embryotoxic effects when administered orally to rats at doses of approximately 100 mg/kg of body weight. Thresholds on the teratogenic potential for man of MCPA or of other phenoxy herbicides have not been established.

The alkyl amine formulation of MCPA was reported by the National Research Council of Canada (1978) to have an LC_{50} (24 h) of 164 mg/L for bluegill. Although no data on the toxicity of the ester formulation were available, in general, the esters of phenoxy herbicides are more toxic than other formulations. The esters of phenoxy herbicides are, however, reported to be rapidly hydrolysed to the less toxic acid. Smith and Hayden (1980) reported the hydrolysis of MCPA esters to the free acid within a few days. Microbial action on the acid to yield humic substances is the primary route of breakdown. The National Research Council of Canada (1978) reports a half-life of MCPA from a few days to a few weeks when conditions favour microbial activity. Cold water and anaerobic conditions were found to decrease the rate of degradation.

Although used extensively in the La Salle River watershed (Cowan and Therrien-Richards, 1986), MCPA was not detected in any

of the surface water, sediment, fish or macrophyte samples from either the La Salle or Assiniboine rivers. The high detection limit of 10 ug/L obtained by the Environmental Protection laboratory in Edmonton may have precluded the quantification of MCPA in the samples. MCPA was quantified by Frank and Sirons (1980) in a survey of stream waters in Ontario; the maximum concentration detected was only 0.3 ug/L. Losses to stream water were correlated to spray activities adjacent to streams. Runoff water, especially when storms occurred near the time of application of the herbicide, also contributed to contamination of stream waters (Frank and Sirons, 1980). Williamson (1984) reported measurable quantities of MCPA in surface waters in Manitoba; the maximum level detected was again 0.3 ug/L. Gummer (1979) reported that 400 tests performed for MCPA in Western Canada did not reveal the presence of MCPA in concentrations above 0.2 ug/L in the surface water. The National Research Council of Canada (1978) reported that phenoxy herbicides, in addition to having a short persistence in the environment, could be concentrated from water by algae and benthic invertebrates. This may partly account for the failure to detect MCPA in the surface waters of the La Salle and Assiniboine rivers.

No maximum acceptable or objective concentration has been adopted for MCPA by Health and Welfare Canada (1979) in its

guidelines on drinking water quality. Health and Welfare Canada however recommended that daily consumption of 2 litres of water by humans should not result in the ingestion of more than 20 percent of the acceptable daily intake (ADI) value for a particular pesticide as published by the World Health Organization or the U.S. Environmental Protection Agency. The National Academy of Sciences (1977), an advisory body to the U.S. Environmental Protection Agency, has recommended an ADI for MCPA of 0.00125 mg/kg/day. Calculation of 20 percent of the ADI would result in an acceptable concentration in drinking water of 8.75 ug/L for MCPA. To properly assess the suitability of the La Salle River water as a potable water supply, an analytical detection limit lower than that obtained by the Environmental Protection laboratory is required. Because of the toxicity of MCPA to aquatic organisms and its potential bioaccumulation by algae and benthic invertebrates, monitoring of MCPA levels in both water and aquatic organisms should be periodically undertaken.

4.5 Trifluralin

Trifluralin, the common name for a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine, controls grass and broad-leaf

weeds in various crops. It is a pre-emergent herbicide that must be soil incorporated within 24 hours of application using equipment that will mix the soil properly. Application and incorporation can be preplant, postplant, with or after the last cultivation of the crop. Trifluralin can be applied by ground or aerial equipment, at rates from 0.6 to 1.1 kg/ha. Although readily soluble in non-polar solvents, trifluralin has a low water solubility of 100 ug/L (Environment Canada, 1984). The emulsifiable concentrates are therefore usually formulated with water as a carrier, but these may also be impregnated on dry fertilizer or applied in fluid fertilizer. Granular formulations are also available.

The Herbicide Handbook Committee, WSSA (1983) reported that trifluralin is strongly absorbed onto soil and shows negligible signs of leaching. This trend was also observed by Davidson et al. (1980) who reported the potential of trifluralin to bind to the soil matrix. The percentage of binding was highest for low concentrations of the herbicide and with increased organic matter in the soil. Phytotoxicity decreased with increased organic content of soils (Pritchard and Stobbe, 1980).

Crop injury from one growing season to the next as a result of carry-over is a problem with trifluralin. Manitoba Agricul-

ture advises that damage to some crops, for example wheat, can occur if the the land has been treated during the previous 21 months and if the amounts of precipitation during that period have been abnormally low. Hayden and Smith (1980) also reported that in heavy clay and sandy loam soils, 36 percent of the applied herbicide was present 10 weeks after application, and that 21 percent remained after 20 weeks.

Williamson (1984) reported the detection of trifluralin in the surface waters of the La Salle River at levels ranging from less than 0.05 to 0.24 ug/L. He postulated that the presence of trifluralin was a result of snow-melt and autumn rainfall events. Willis et al. (1975) also reported that even with proper use of trifluralin on agricultural lands, high concentrations in runoff were associated with rainstorms that occurred within one week after application. Trifluralin was not detected in any of the surface water samples from the La Salle River in this study.

Trifluralin may not have been detected due to the fact that precipitation was below normal in May (pers. comm., Environment Canada), the month during which trifluralin would have been applied. In June, when precipitation was above normal (pers. comm., Environment Canada), the amount of trifluralin available for leaching into runoff would be greatly reduced due to plant

absorption and adsorption onto soil.

The presence of trifluralin in the ecosystem can be detected from other than water analyses (Chapman et al., 1982). Insoluble and slightly soluble pesticides, such as trifluralin, tend to be readily adsorbed to sediment and particulate matter, accumulating in the sediment. Although trifluralin was not detected in the surface water, it was detected in one sediment sample from the La Salle River, Site 4A, at a level of 4 ng/g and in one sediment sample from the Assiniboine River, Site 9A, at 6 ng/g. Trifluralin residues were also detected in fish in concentrations ranging from 4.5 to 7.5 ng/g (Table 8).

Table 8. Concentration of trifluralin (ng/g) in fish

Site No.	Sampling Date	Fish Specie	Concentration (ng/g)
1	-	Brown Bullhead	4.5
2	14 Aug 84	Brown Bullhead	4.6
4A	20 Sept 84	Stickleback	4.7
4B	-	Central Mudminnow	7.5
4C	-	Brown Bullhead	5.7
6B	9 Sept 84	Central Mudminnow	ND[1]

1. ND = Not Detected

In a study of trifluralin contamination in a river system, Spacie and Hamelink (1979) reported that trifluralin was accumulated in fish by direct uptake from water. The residues were proportional to the concentration in the river water. A mean concentration of 1.8 ug/L of trifluralin in river water resulted in mean residue concentrations in whole fish ranging from 3.24 to 10.78 mg/kg (Spacie and Hamelink, 1979). These values corresponded to bioconcentration factors of 1800 to 6000, depending on the species of fish. Yockim et al. (1980) also investigated the behaviour of trifluralin in an aquatic model ecosystem and reported bioaccumulation for the aquatic organisms tested. After 30 days of exposure to a continuous dose of 100 ppm trifluralin in the ecosystem, the bioaccumulation ratios were 878, 3961, and 3919 for snails, algae and fish respectively. Bioconcentration factors for trifluralin in fish from the La Salle River cannot be calculated since trifluralin was not quantified above the analytical detection limit of 0.10 ug/L. The results of Table 8 however suggest that even trace levels of trifluralin in the surface water can bioconcentrate in the biota.

Trifluralin is reported to have a low toxicity to mammals. The acute oral LD_{50} for rats is greater than 10,000 mg/kg and is greater than 2,000 mg/kg for rabbits, chickens and dogs. In 2-year feeding trials, rats receiving 2000 mg/kg and dogs receiving

1000 mg/kg in diet suffered no ill effects (Glasshouse Crops Research Institute, 1979). Aquatic organisms appear to be more sensitive than mammals to trifluralin (Environment Canada, 1984); the LC_{50} (96 h) for Bluegill ranged from 0.047 to 0.070 mg/L. Rainbow trout were slightly less tolerant, with an LC_{50} (96 h) of 0.026 to 0.062 mg/L. Daphnia magna exhibited greater tolerance, with LC_{50} (96 h) concentrations ranging from 0.320 to 1.0 mg/L (Environment Canada, 1984). Rohde et al. (1980) felt that surface and subsurface losses of trifluralin residues under rainfall or snowmelt conditions could possibly result in levels approaching those which are toxic to aquatic organisms. He recommended the establishment of a buffer strip or vegetated waterway adjoining cropping areas to significantly reduce trifluralin movement from the site of application into surrounding streams.

Trifluralin is a suspected carcinogen. Gosselin et al. (1984) reported that female mice ingesting 2740 ppm for 78 weeks showed a 28 percent incidence of hepatocellular carcinoma. This carcinogenic activity was possibly due to N-nitrosodi-n-propylamine, a contaminant in the technical grade trifluralin (Gosselin et al., 1984). Sittig (1985) has also described trifluralin as a carcinogen.

Although mammalian toxicity is low, the bioaccumulation

potential of trifluralin and its suspected carcinogenicity, make the presence of this herbicide in drinking water a particular concern. Health and Welfare Canada has not adopted a maximum acceptable concentration in drinking water. The National Academy of Sciences (1977) recommended an acceptable daily intake of 0.1 mg/kg/day, which corresponds to a concentration in drinking water of 35 ug/L, based on a daily consumption of 2 litres by a 70 kg person. This value was based on acute and chronic toxicity data and did not include the more recent data on carcinogenicity and bioaccumulation. A lower acceptable concentration in drinking water might be expected if the more recent data were considered in a re-evaluation of the herbicide.

4.6 Triallate

Triallate, or S-2,3,3-trichloroallyl diisopropylthiocarbamate, is recommended for control of wild oats in barley, wheat, oilseeds and peas by Manitoba Agriculture. It is incorporated into the soil at the rate of 1.0 - 1.5 kg of active ingredient per hectare as a pre-sowing or pre-emergent treatment. Application can also be made in the fall within 3 weeks of soil freeze-up for spring-planted wheat and barley (Herbicide Handbook Com-

mittee, WSSA, 1983).

The persistence of triallate when applied as an emulsifiable concentrate in Canadian soils was studied by Smith (1982). He reported that applications at the rate of 1.7 kg/ha resulted in persistence of 3 - 35 percent of the amount applied after 22 weeks and of 0 - 12 percent after 72 weeks. Smith (1982) also reported that the carry-over of granular formulations of triallate in a heavy clay soil was approximately twice that of the emulsifiable concentrate. This difference was attributed to a greater loss of triallate to the atmosphere from the more volatile emulsifiable form. Smith and Milward (1985) also studied the rates of breakdown of triallate residues in clay soil and determined that half-life values ranged from 37 to 45 days.

Triallate was not detected in any of the surface water samples from the La Salle or Assiniboine rivers using a detection limit of 0.10 ug/L. This may be due to the fact that losses of triallate from the soil by leaching are less extensive than for pesticides having high water solubilities and low adsorptions to soil. Triallate has a water solubility of only 4 ppm at 25^{o} C (Weed Science Society of America, 1983) and is strongly adsorbed to soil or organic matter. Field leaching of triallate by rainfall was not detected by Smith and Hayden (1976) when soil incor-

porated at a rate of 1.7 kg/ha, a rate slightly higher than that recommended for agricultural use.

Williamson (1984) however reported the presence of triallate in all surface water samples collected from the La Salle River in levels ranging from trace to 0.10 ug/L using an analytical detection limit of 0.05 ug/L.

Although triallate was not detected in the water column, it was detected in fish in values ranging from 3.3 to 9.2 ng/g (Table 9) and in the bottom sediments from 16.9 to 119 ng/g (Table 10). The low water solubility of triallate and its tendency to adsorb to soil or organic matter account for its presence in the sediment. Sediment accumulation of contaminants does not result in complete protection of the aquatic environment. Sediments can slowly release trace contaminants to the water column, where they can be uptaken by aquatic biota. The results indicate that even at low levels in the aquatic environment, bioconcentration of triallate in the biota is occurring. In order to determine a bioaccumulation factor in fish from the water column, a lower analytical detection limit than 0.10 ug/L for triallate in water is required.

Triallate levels (Table 10) were noticeably higher than tri-

fluralin levels in sediment. This could be in part because more triallate was used and by a larger percentage of farmers in the La Salle River watershed (Cowan and Therrien-Richards, 1986). Twenty-seven percent of farmers surveyed were reported to have applied approximately 11,000 litres of Treflan, a trifluralin

Table 9. Concentration of triallate (ng/g) in fish

Site No.	Sampling Date	Fish Specie	Concentration (ng/g)
1	-	Brown Bullhead	4.0
2	14 Aug 84	Brown Bullhead	ND[1]
4A	20 Sept 84	Stickleback	3.3
4B	-	Central Mudminnow	ND
4C	-	Brown Bullhead	4.2
6B	9 Sept 84	Central Mudminnow	9.2

1. ND = Not detected

Table 10. Concentration of triallate (ng/g) in sediment

Site Number	Triallate (ng/g)
2C	31.9[1]
3A	30.2[1]
3C	31.7[1]
4A	96
4B	16.9[1]
4C	36.1[1]
5A	24.7[1]
5B	119.0[1]
5C	21.3[1]
9A	ND[2]

1. May be interference
2. Not detected

product, whereas 42 percent of farmers used 40,000 litres of a liquid formulation and 18,000 kg of a granular formulation of triallate. Although leaching of triallate due to rainfall was not reported to be a significant method of offsite transport from the site of application (Smith and Hayden, 1976), triallate which had adsorbed onto soil particles may have been transported along with soil particles into the aquatic environment. Erosion of soil by wind in the drier summer months may have also contributed to the offsite movement of triallate. Sediment accumulation of triallate in this manner could eventually result in slow release to the water column and ultimately be uptaken by aquatic biota.

Generally, mammalian toxicity to technical grade triallate is low. The oral acute LD_{50} for bobwhite quail (Colinus virginianus) was reported to be greater than 2251 mg/kg and in the range of 1675 - 2165 mg/kg for rats (Meister, 1984). The Herbicide Handbook Committee, WSSA (1983) also reported that there was no evidence of subacute toxicity in a 90-day feeding study with mice at 30 mg/kg/day. Two-year chronic toxicity feeding studies with rats and dogs were also conducted. Results indicated that triallate was not carcinogenic and no evidence of chronic toxicity was observed at dosage levels of up to 15 mg/kg in dogs.

Aquatic organisms exhibited greater sensitivity to triallate than mammals. The Herbicide Handbook Committee, WSSA (1983) reported 96-hour LC_{50} in bluegill and in rainbow trout of 1.3 and 1.2 mg/L respectively. The 48-hour LC_{50} value for Daphnia magna was only 0.43 mg/L.

Guidelines for maximum permissible amounts of triallate in surface waters or in drinking water have not been established by the federal or provincial governments. Williamson (1986) recommends objective surface water concentrations for pollutants that are persistent or have accumulative effects to be less than 0.01 of the 96 hr LC_{50}. Using the 96 hr LC_{50} for rainbow trout, this results in an objective concentration of 0.01 mg/L. The provinces of Alberta and Saskatchewan define reasonably safe concentrations of pesticides in their multi-purpose water quality objectives as 1/100th of the 48-hour TLM (50% kill of organisms in 48 hours) (Canadian Council of Resource and Environment Ministers, 1985). Using the LD_{50} value for Daphnia magna, this results in a reasonably safe concentration of less than or equal to 4.3 ug/L for triallate. The values of triallate in the surface water of the La Salle River are well below both these objective concentrations and yet, evidence of bioaccumulation in the fish is present.

4.7 Diclofop-Methyl

Diclofop-methyl is the methyl ester of diclofop, the common name for 2-(4-(2,4-dichlorophenoxy)phenoxy)propionic acid. It was introduced to the market in 1975 as a post-emergent herbicide effective for the control of annual grasses (Glasshouse Crops Research Institute, 1979). Diclofop-methyl does not translocate readily within the plant and coverage is therefore an important factor for good weed control. Application at the rate of 1.12 kg/ha is recommended when grasses are at the 2 - 4 leaf stage of growth (Herbicide Handbook Committee, WSSA, 1983). Its primary use is on the cereals barley, wheat and rye, and on the oilseeds. Lentil, peas, sunflowers and field beans are also tolerant.

Under aerobic conditions, the diclofop-methyl ester is reported to hydrolyse in the soil to the acid within a matter of days. The acid is then metabolized rapidly with a half-life of 10 days in sandy soils and approximately 30 days in sandy clay soils (Herbicide Handbook Committee, WSSA, 1983). Martens (1978) and Gaynor (1984) reported similar results. Martens indicated that 50 percent loss of diclofop occurred within 6 - 9 days in sandy soil and in 23 - 38 days in sandy loam. The La Salle River watershed is comprised dominantly of sandy loam and clay loam soils. Microorganisms in the soil were the active agents in the

degradation process. Gaynor (1984) reported that less than 14 percent of the original concentration applied remained at the end of the growing season. Carry-over of phytotoxic residues was not observed from one growing season to another. Gaynor (1984) further noted in his study the dependence of the rate of hydrolysis of the ester to the acid on pH. A lower pH decreased the rate of hydrolysis and subsequent degradation.

Diclofop-methyl is water soluble at the rate of 0.3 g/100 mL and is, therefore, not readily leached by rainfall. Manitoba Agriculture (1986) recommends a rain-free period of only one hour after application to maximize weed control. The Herbicide Handbook Committee, WSSA (1983) also concluded that diclofop-methyl does not leach downwards or move laterally in the soil. This conclusion was based on studies that revealed that diclofop-methyl, when applied at the rate of 3.4 kg of active ingredient per hectare, was detectable in the 0 - 7.6 cm soil level, and only occasionally detectable in the 7.6 - 15 cm level at low concentrations, at harvest time.

Diclofop-methyl was quantified in the August, September and December surface water samples of the La Salle River from 0.10 to 0.58 ug/L (Table 10). It was not detected in the Assiniboine River samples, nor was its presence measured in the macrophyte,

fish or sediment samples. Diclofop-methyl, similarly to other phenoxy herbicides such as 2,4-D and MCPA, is not persistent in the environment and would, therefore, not be expected to appear in fish, sediment or macrophyte samples. It does, however, persist in the soil, adsorbed to soil particles, for sufficient time to be transported offsite into nearby streams and rivers.

Table 11. Concentration of diclofop-methyl (ug/L) in surface waters

Sampling Date	Station No. 1	2	3	4	5	6	7	8	9
13 Aug 84	ND[1]	0.32	0.58	0.10	ND	ND	ND	ND	ND
18 Sept 84	ND	0.15	0.22	0.12	ND	0.22	ND	ND	ND
17 Oct 84	ND	ND	ND	ND	ND	ND	ND	ND	ND
13 Nov 84	ND	ND	ND	ND	NR[2]	ND	ND	ND	ND
18 Dec 84	ND	ND	0.12	ND	0.18	ND	ND	ND	ND

1. ND = Not Detected
2. NR = No Result

Chlorophenoxy herbicides generally are assumed to degrade rapidly in aquatic systems under aerobic, warm water conditions. However, diclofop-methyl was detected in samples collected in

December, 1984, suggesting that diclofop-methyl is more resistant to degradation in cold water and under possible anaerobic conditions, a trend also observed with other phenoxy herbicides (National Research Council Canada, 1978).

Mammalian toxicity studies indicate that diclofop-methyl is low in toxicity. The oral LD_{50} for the technical product was reported as 557 - 580 mg/kg for rats and greater than 1600 mg/kg for dogs. Avian studies on bobwhite quail resulted in an acute oral LD_{50} value of 4400 mg/kg. A three-generation reproduction study on rats was also performed with a no-effect level of 30 ppm reported. Mutagenicity was not observed in two studies using the Ames test with four bacterial strains in dose ranges up to 5 milligrams (Herbicide Handbook Committee, 1983).

Aquatic studies were also performed. The LC_{50} (96 h) for rainbow trout and for carp were 1.38 and 2.60 ppm respectively for a diclofop-methyl formulation. The LC_{50} (48 h) for Daphnia was slightly greater at 4.03 ppm (Herbicide Handbook Committee, 1983).

A maximum acceptable concentration has not been established for the presence of diclofop-methyl in drinking water by Health and Welfare Canada. Manitoba's proposed surface water quality

objectives (Williamson, 1986) state that the concentration of pollutants that are not persistent should not exceed 0.05 of the 96 hr LC_{50}. Using toxicity data for rainbow trout, this results in a surface water quality objective of 0.07 mg/L for diclofop-methyl. None of the values detected in the surface waters of either the La Salle or Assiniboine rivers exceeded this concentration. The low levels of diclofop-methyl detected (Table 10) should therefore not pose a threat to users of the surface waters. There is inadequate information available on diclofop-methyl, however, to properly assess the significance of low-level exposures to health.

5. Conclusions and Recommendations

Herbicides that are applied in significant quantities by farmers in the La Salle River area are being transported from the site of application into neighbouring streams and rivers. The transportation mechanisms appear to be complex. Generally, the acid herbicides, namely dicamba, bromoxymil, 2,4-D and diclofop-methyl, were detected in the surface waters of the La Salle and Assiniboine rivers in the 0.1 to 4.0 ug/L range. MCPA was not detected in the surface water, possibly because of its high detection limit.

Although trifluralin and triallate were not detected in the water column, bottom sediment samples from both the La Salle and Assiniboine rivers contained from 4 to 119 ng/g of these pesticides. Fish samples also revealed the presence of both these pesticides in concentrations from 3.3 to 9.2 ng/g. These results suggest that even at low levels in the water, these two pesticides can bioaccumulate in the biota.

It was not possible to calculate the bioaccumulation factors of trifluralin and triallate because if any of these herbicides were in the water column, their levels were below the detection limit.

In general, there is inadequate scientific data to determine the effects to aquatic organisms or to man from low level exposure to the various herbicides which were quantified in the La Salle and the Assiniboine rivers. Many studies on degradation have been conducted only under warm weather conditions and have not considered the reduced rate of degradation in a continental sub-arctic climate. Additional information on the persistence of herbicides under cold water conditions and their effects in the aquatic ecosystem at low levels is required.

From the limited data, it appears that the concentrations of the various acid herbicides detected in the water column do not pose a significant threat to humans. The concentrations of pesticides in both the La Salle and Assiniboine rivers were below the recommended levels in drinking water that have been established by Health and Welfare Canada, or where maximum acceptable concentrations have not been established, were less than the acceptable daily intake values set by the U.S. Environmental Protection Agency or the World Health Organization. There is concern however with the presence of trifluralin and triallate in the sediment and fish. Analyses for these compounds in the water column at much lower detection levels than used in this study are required to calculate the bioaccumulation factors for

these chemicals and to determine acceptable concentrations in the water column for multi-purpose water use, including the use as a potable water supply. Health and Welfare Canada (1979) has recommended an objective concentration of 0.05 ng/L for chlorinated hydrocarbon pesticides which tend to persist in the environment. This same value should be considered as the objective concentration for trifluralin and triallate in drinking water.

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